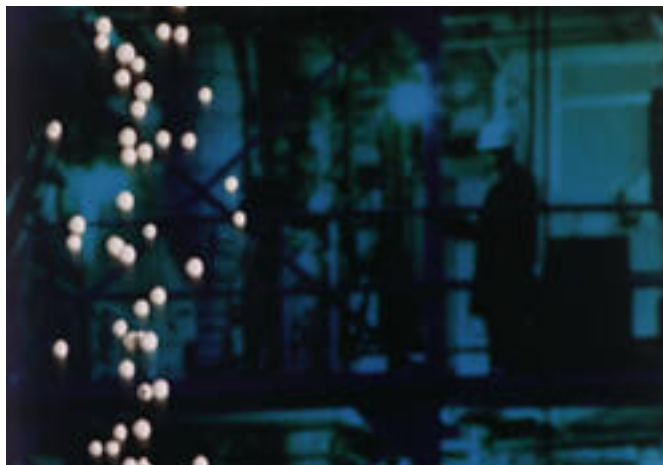# Modified Retorting for Waste Treatment

We are developing a technically sound, environmentally benign, and economically feasible retorting system, which uses a bed of hot ceramic spheres as the heat carrier, for decomposing hazardous wastes.

THE Laboratory has a number of programs to develop advanced technologies for environmental cleanup and waste treatment. In these efforts, existing LLNL technologies are being modified or adapted and new technologies are being developed to address pressing environmental issues. One such technology is retorting, in which the Laboratory has more than two decades of experience.

Retorting is the process by which substances are distilled or decomposed by heat, such as oil from oil shale, metal from ore, or gas from coal. Our retorting technology has focused on recovering oil from oil shale (see the box on p. 5 for a description of our oil-shale work). During the course of this work, we developed the LLNL hot-recycled-solid (HRS) retorting process, a rapid retorting system that uses hot recycled oil shale as the solid heat carrier (see the box on p. 9). We are now adapting the HRS process to address pressing problems in the field of waste treatment.

Evolution of the New Retorting System

During the course of our oil-shale work, we realized that the HRS process, if modified and extended, can be applied to several important problems in the field of waste treatment and environmental cleanup. For example, a preliminary laboratory study showed that the HRS process might be suitable for removing organic compounds and for decomposing sodium nitrate ($NaNO_3$). Organic compounds and sodium nitrate are major constituents of the mixed waste stored in underground tanks at the Hanford, Washington, facility. (Mixed waste is both radioactive and chemically hazardous.)

In 1993, we began to modify our on-site pilot plant that was built for processing oil shale. We have now adapted this pilot plant and are collaborating with researchers elsewhere to demonstrate the feasibility of pretreating Hanford tank wastes using a circulating bed of hot ceramic spheres. At the same time, we are pursuing several other applications of an HRS retort process for treating a variety of substances of environmental concern. We are demonstrating that the HRS process has potential applications for decomposing or treating many of the

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harmful chemicals and compounds found throughout and beyond the DOE complex.

Advantages of Thermal Treatment

Maintaining a clean environment requires innovative techniques for treating and disposing of toxic substances. In recent years, LLNL researchers have developed several alternatives to long-term storage, landfill, or incineration. Some of our ideas come from basic research. Others, like the modified HRS process, are created by adapting an existing technology for a new application.

The modified HRS process applies heat to convert waste in a liquid state into nontoxic products. In thermal treatment, a high-temperature reducing atmosphere (that is, one with no oxygen present) is used to convert organic matter and other hazardous waste materials into a volatile vapor phase. Following thermal treatment, the volatiles are subjected to steam reforming, a process in which high-temperature (–1000°C) steam is applied to break down the volatiles into simpler, nontoxic species. After thermal treatment is applied to a large volume of waste sludge, all that remains is a small amount of ash. The volume reduction is considerable, ranging from 50 to 70 times less volume than the starting material.

Thermal treatment in the absence of oxygen has several other advantages beyond a large decrease in waste volume. For example, pyrolysis processes do not produce such highly undesirable products as dioxins and furans.

Thermal treatment involves one or more endothermic reactions. That is, the chemical reactions that take place absorb rather than generate heat. Such a process can be stopped immediately simply by shutting off the heat source. This safety feature is another reason that thermal decomposition is preferable to incineration for waste treatment. In addition, our HRS process operates at atmospheric pressure, providing enhanced worker safety. It also accommodates variable types of wastes—an important consideration for the different applications we have in mind.

Our HRS process uses a circulating bed of heated ceramic spheres, shown in Figure 1, as the heat carrier. We heat the ceramic spheres (using electric heat) until they reach a temperature that can vaporize and process the liquid sludge fed into the system. This technique—spreading out the liquid waste over the very large surface area afforded by the hot ceramic spheres—provides sufficient time for thermal treatment and avoids the problems of clumping and agglomeration that can occur when waste is treated alone.

In recent years, thermal treatment technology has advanced considerably as an economical alternative to incineration. Figure 2 diagrams a commercial, mobile detoxifier unit that can be used to treat gases, liquids, and solids. This unit handles waste in three ways:
• Industrial hazardous waste can be drum-fed or pumped from tanks.
• Medical waste, such as needles, gowns, and other contaminated solids, can be shredded and screw-fed counter to the flow of hot reactor gases.
• Liquid and slurried waste can be fed and processed in a circulating bed of ceramic spheres.

Compared to the disposal costs associated with incineration or landfill,

Figure 1.
Photograph of the ceramic spheres (0.6 cm in diameter). In our pilot plant, these ceramic spheres are heated to and maintained at 555°C. Liquid waste is sprayed onto the spheres, and as they are circulated in a moving packed-bed reactor, they provide the energy required to thermally decompose the waste.

this commercial unit is a more economical alternative. Nevertheless, units on the market today cannot handle some types of hazardous waste or the mixed wastes plaguing the DOE complex.

Our goal is to develop the HRS system using hot ceramic spheres into a robust and highly reliable process for decomposing hazardous liquid waste, sludges, and contaminated soils.

The HRS process can then be used to pretreat mixed waste (decomposing the chemically hazardous components, so the waste can be disposed of as radioactive-only waste).

HRS Process for Decomposing Sodium Nitrate

The 177 underground storage tanks at the Hanford facility contain various mixed wastes in the form of radioactive isotopes, organic chemicals, and sodium nitrate. The sodium nitrate in the tanks is a result of using the Purex process (which involves adding nitric acid) for extracting uranium from ore. When the waste materials were prepared for underground storage, sodium hydroxide was added to neutralize and buffer the acid solution and thereby reduce the likelihood that
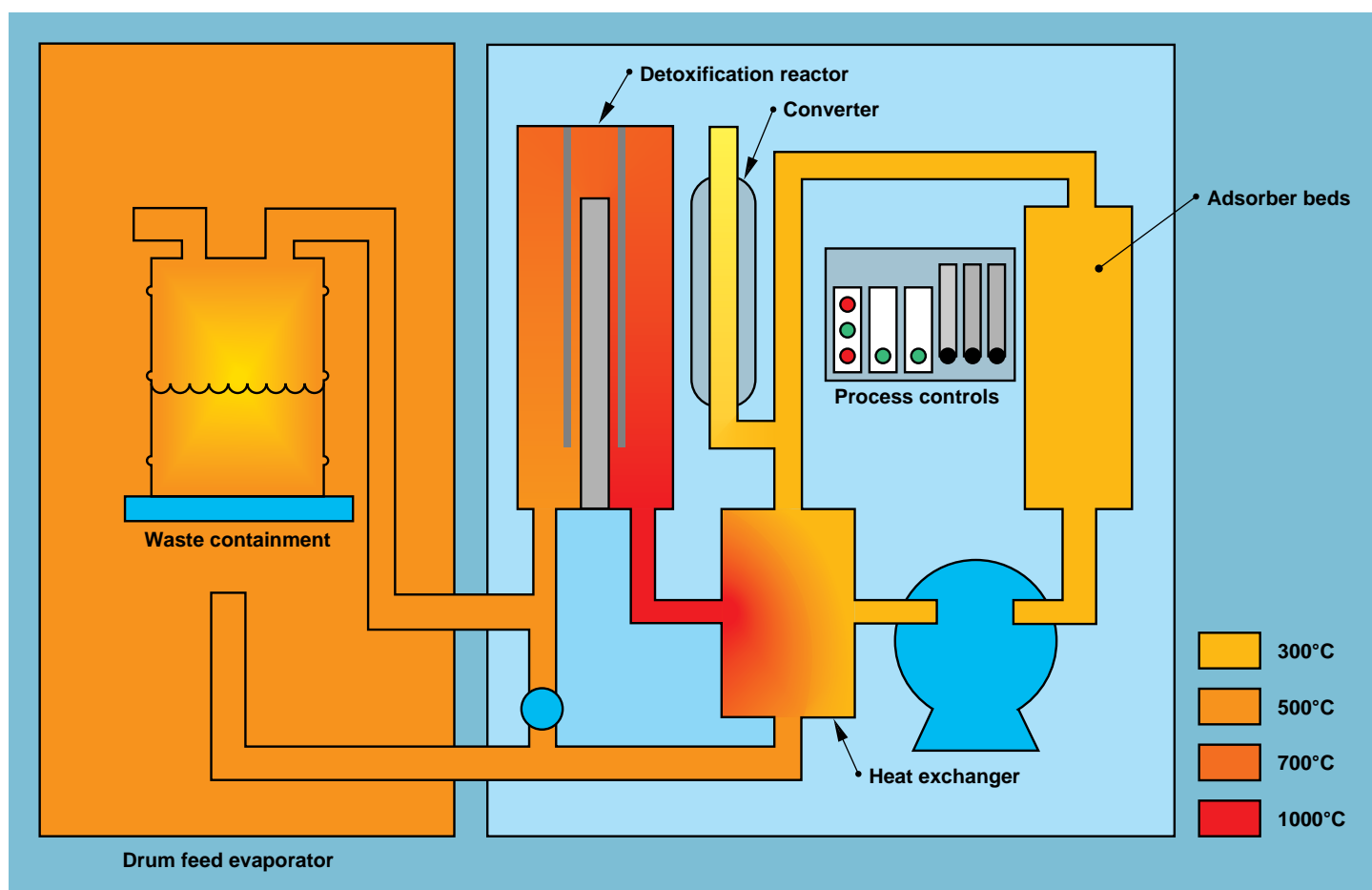

Figure 2. Diagram of the Synthetica Detoxifier, manufactured by Synthetica Technologies, Inc., of Richmond, California. This unit uses a multistep process to detoxify gases, liquids, or solids. Waste, such as liquid organics or shredded solids are vaporized in the evaporator (a drum feed is shown on the left in this example). Organic vapors are destroyed in the detoxification reactor shown on the right. The reactor uses electrical heat and has no fuel flame. The heat exchanger recirculates excess heat to the feeder. The converter oxidizes detoxified gases to CO_2 and H_2O. Activated carbon in the adsorber beds removes trace organics and metals. After thermal treatment of waste, a relatively small amount of dry, solid residue remains in disposable drums or can be steadily discharged, depending on the specific operation. Destruction levels are 99.99% or greater.

the storage tanks would leak over time. Nitric acid and sodium hydroxide, which are each highly corrosive, react to produce sodium nitrate. Despite the precautions taken to minimize risk, the tanks are now leaking, and there is concern that the contents will eventually contaminate the Columbia River (see Figure 3).

To solve this problem, the hazardous waste material—the organic wastes and sodium nitrate—must first be separated from the radioactive material. Once we rid the tanks of organics and sodium nitrate, the radioactive waste stream—in the form of a solid residue—can be processed in a vitrification plant to yield a glass waste product. Encapsulating radioactive compounds in either a ceramic or silica glass will prevent them from leaching into the environment for very long periods of time.

Preliminary Laboratory Study

The thermal decomposition of sodium nitrate is a complicated issue in itself. A wide variety of reactions and products are possible depending on temperature, the kinds and amounts of reducing gases that are added, and many other factors. The presence of steam, for example, is an essential component of our system because, without steam, unwanted solid products are formed (for example, peroxides and superoxides of sodium).

We performed a preliminary laboratory study to define some of the conditions needed to decompose sodium nitrate in a pilot plant using our modified HRS process. One of our main objectives during this study was to establish the optimum temperature at which more than 95% of the sodium nitrate is decomposed in less than 10 minutes. We also wanted to understand the kinds and relative amounts of product gases that would be generated.

We found that sodium nitrate could be almost completely decomposed under controlled laboratory conditions in less than 10 minutes at about 555°C. As a result, we chose 555°C as the operating temperature of our pilot plant.

The principal nitrogen-containing gas products from decomposition of sodium nitrate in the presence of steam and carbon dioxide (CO_2)

Figure 3. Aerial view of the Hanford, Washington, facility and its proximity to the Columbia River. This historic photo was taken on September 25, 1944. Mixed waste is now stored in 177 underground tanks at Hanford. Over time, the leaking contents could contaminate the Columbia River. Solving the problem involves several steps. With our modified HRS process, we can initiate remediation by separating the organic wastes and sodium nitrate in the tanks from the radioactive material they contain. The radioactive solids can then be encapsulated in a ceramic or silica glass to ensure environmental protection.
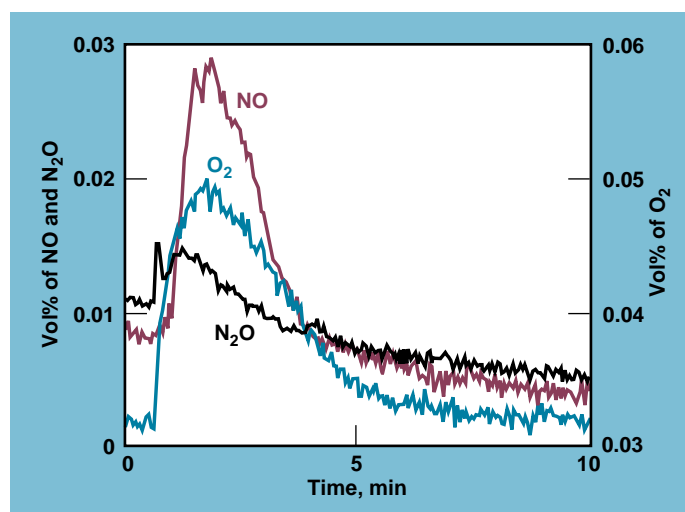
Figure 4. The evolution of several product gases from decomposing sodium nitrate over the course of 10 minutes. The figure shows the vol% of NO, N_2O, and O_2 of the total gas that is flowing through the fluidized bed. In this particular laboratory experiment—one of several in a series—we injected steam and argon, and the reaction was carried out at 555°C. This test showed that all the gases evolved similarly, and the sodium nitrate was decomposed in less than 10 minutes. This experiment established the temperature at which we would need to operate a pilot plant for decomposing sodium nitrate.

were determined by mass spectrometry to be:

- 70% NO.
- 15% N_2O.
- 5% NO_2.
- 5% N_2.
- 5% unreacted.

Figure 4 shows the evolution of several of these product gases from sodium nitrate over the course of 10 minutes. These mixtures of nitrogen-containing gases are of varying environmental concern and would have to be "scrubbed" prior to venting to the atmosphere. Scrubbing is a relatively straightforward process that can be done by chemical treatment or using a catalytic converter similar to those in automobiles.

The principal solid product of sodium nitrate thermal decomposition, in the presence of CO_2, is sodium carbonate (Na_2CO_3). This is an acceptable solid product. When processed in a vitrification plant, sodium carbonate would be converted to sodium silicates so that only CO_2 would be released into the atmosphere.

Demonstration at the LLNL Pilot Plant

In the fall of 1993, we applied what we had learned about sodium nitrate decomposition in the laboratory to larger-scale tests. In collaboration with researchers at Sandia National

LLNL's Work on Oil-Shale Processing

Interest in oil-shale retorting stems from the vast deposits of oil shale in the western states. The shale basins in Colorado, Utah, and Wyoming are the largest and richest oil shale deposits known, rivaling the petroleum reserves in the Persian Gulf. However, producing liquid fuel from western U.S. oil shale requires a technically sound and environmentally benign retorting system that can handle very large volumes of solids.

Several oil-shale processes developed by others in the 1970s were technically successful (i.e., they produced oil), but they proved to be too expensive for commercialization. Industry development of oil-shale retorting has been inhibited by the return to lower oil prices in the 1980s, uncertainty in the future price of crude oil, and the long lead time for commercializing new technology.

Our initial work on oil-shale processing, in the 1970s, focused on *in situ* technology. In the early 1980s, our efforts shifted to the broader field of advanced, aboveground oil-shale retorting. During the course of this work, we developed the LLNL hot-recycled-solid (HRS) retorting process. Retorts using hot solids as the heat carrier, as does our HRS process, have many advantages over earlier hot-gas retorts. For example, methods using hot solids are:

- Faster (minutes vs hours for heating).
- Yield more oil due to rapid heating (10–15% improvement).
- More energy efficient (use all the available carbon).

In addition, hot-solid retorts can:

- Process smaller particles, greatly reducing the heat-up time from hours to minutes.
- Process fines (particles smaller than about 0.5 mm in diameter that are thrown away by hot-gas retorts).
- Reduce environmental impact because of the self-scrubbing of sulfur.
- Be more easily scaled up to the large systems needed for a commercial plant.

In early 1991, we signed a three-year cooperative research and development agreement (CRADA) with Amoco Corporation, Chevron-Conoco Shale Oil Semiworks Joint Venture, and Unocal Corporation. Under this agreement, the first of its kind for LLNL, we continue to advance oil-shale technology and to explore ways to reduce the cost of producing liquid fuels from oil shale. This CRADA is now in its third year. During this time, we have developed a commercial concept that can:

- Produce oil from shale.
- Generate electric power.
- Produce high-value specialty chemicals (e.g., dyes, waxes, perfumes, and an asphalt additive that extends the life of roads, to name a few).

Our concept makes shale-oil processing economical at a modest scale of 10,000 barrels per day. We are currently seeking additional funding to continue with the work required to develop the technology fully for commercial application.

Laboratories–California, we adapted our on-site oil-shale pilot plant to demonstrate the feasibility of decomposing sodium nitrate in a small working-model system. Our demonstration tests were scaled to process approximately 1 to 2 kg per hour of liquid waste. (This rate is roughly one-hundredth the rate at which we would process actual waste in a commercial-scale plant.) Our tests lasted about four hours each day for four consecutive days.

Figure 5 shows the simplified HRS system we used to demonstrate sodium nitrate decomposition. Keep in mind that this modified system differs in several important ways from the system we developed earlier for oil-shale processing (compare Figure 5 with the illustration in the box, p. 9). To extract oil from shale, we needed air (oxygen) to burn the residual carbon and to lift the spent shale up around the loop to the top of the tower. In addition, oil-shale retorting is a solid process (with no added water). In contrast, our waste processing takes place in a reducing atmosphere (no oxygen) and involves liquids, not solids, because the waste in the Hanford drums is already in liquid form.

The main steps in the decomposition cycle for sodium nitrate can be best understood by referring to the principal pieces of equipment in Figure 5:

1. Heater. The moving-bed heater (upper left of Figure 5) heats the ceramic spheres using gas heated by an electric coil together with external wall heaters (not shown). The hot ceramic spheres then transfer their heat to the waste feed to reach a reaction temperature of 555°C.

2. Reactor. Just below the heater, sodium nitrate (the liquid waste to be decomposed) is injected onto the hot ceramic spheres, which then enter a moving packed-bed reactor. Thermal decomposition of sodium nitrate takes place in the reactor as the hot spheres, coated with sodium nitrate liquid, pass through the bed with an average residence time of 10 minutes. Steam and CO_2, injected from below, flow up and around the hot spheres to aid the decomposition and to produce sodium carbonate as the primary solid product.

3. Condensers. Gas and steam in the reactor pass through a cyclone separator and into condensers. The cyclone is a funnel-shaped device that uses centrifugal means to separate the gases and heavier solids. The condensers (at the right of the reactor in Figure 5) collect liquid condensate, which, for sodium nitrate destruction, is mostly water. Noncondensable gas is measured by Fourier transform infrared (FTIR) and mass spectrometry to determine its composition prior to venting.

4. Pneumatic Lift. Below the reactor, an LLNL-developed L-valve dispenses the hot spheres into a pneumatic lift pipe, which transports them to the top of the tower. The L-valve looks something like a miniature set of stairs. This valve uses puffs of compressed gas (such as CO_2 or an inert gas) to regulate the flow of spheres down the steps. The rate of discharge for the L-valve determines the recirculation rate of the spheres and the residence time of the spheres in the reactor. Hot recycled gas, air, or nitrogen is used as the driver gas for the pneumatic lift system. High velocities of the spheres in the lift pipe, as well as particle-particle interactions during pneumatic transport, remove the fine-grained crystalline sodium carbonate from the surface of the spheres, producing a fine dust.

5. Classifier. In the classifier (upper left of Figure 5), the spheres are separated from the lift gas and sent back to the heater. Discharge gas, carrying the small sodium carbonate crystals, passes through a cyclone separator and a dust filter. The solid waste products are collected, and the filtered, clean lift gas is recycled or vented.

During our demonstration tests, the HRS circulation system was operated 5 to 6 hours a day, without major problems. The off-gases were continuously analyzed to quantify the decomposition products of sodium nitrate. The distribution of nitrogen in the four product gases was:
- 70% NO.
- 0% N_2O.
- 30% NO_2.
- 0% N_2.

These results revealed that pilot-plant chemistry is significantly different from that of the controlled laboratory experiments. In particular, higher amounts of NO_2 are produced, and no N_2O was detected. The fact that we observed no detectable N_2O is highly desirable since its absence will aid in the conversion of nitrogen oxides into molecular nitrogen prior to release of gas into the atmosphere.

After examining the solids at the end of each day and following shutdown of the system, we found no signs of sticking, tacking, or agglomeration of the liquid waste. Our analysis showed that more that 95% of the sodium nitrate entering the system was decomposed. The primary solid product was sodium carbonate—the solid that we expected. These products would be converted into sodium silicates in a vitrification plant. From these tests, we concluded that the overall performance of the HRS process for sodium nitrate decomposition is highly promising.

Cold Test at the Sandia Facility

In addition to our pilot plant work, we are collaborating with researchers at Sandia to develop an integrated steam-reforming process for mixed
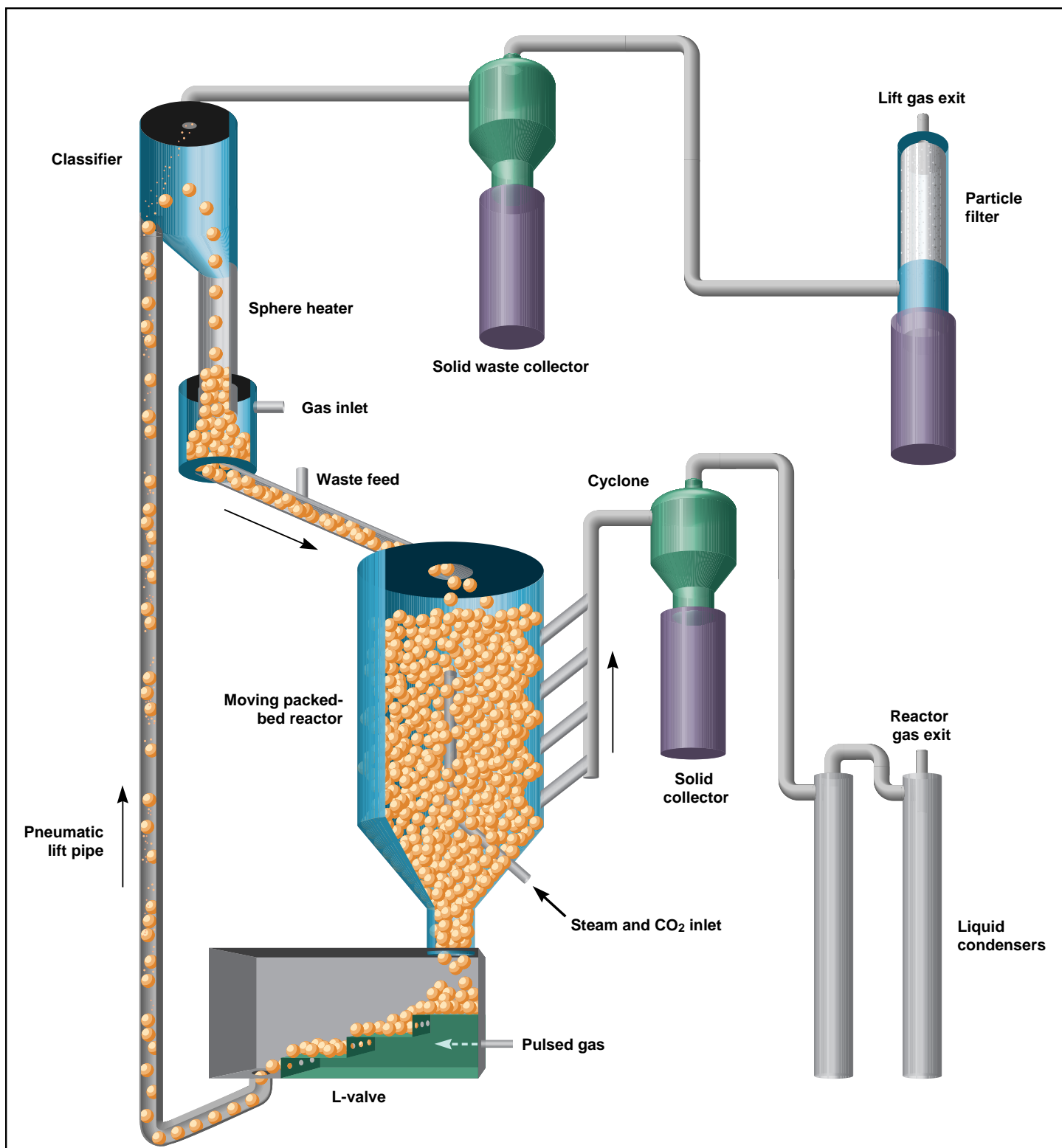
Figure 5. Schematic of the 4-story-tall HRS pilot plant at LLNL used, in October 1993, to demonstrate the decomposition of sodium nitrate. In this system, 50 kg of hot ceramic spheres, fed into the reactor from the heater, provide a large surface area for the thermal treatment and decomposition of sodium nitrate. The spheres are metered from the bottom of the reactor and are recirculated via a nonmechanical pneumatic lift back up into the heater. The off-gases and solids are separated in the classifier, cyclone, and filter (at top). The condensers (bottom right) collect liquid condensate. Noncondensable gas is measured and then vented.

waste. As shown in Figure 6, Sandia has built and is now operating a cold-flow system that can be used to study the functions of various pieces of HRS equipment at a larger scale. This is the next logical step toward a scaled-up waste-treatment HRS system that can be applied to the problem of sodium nitrate and other compounds.
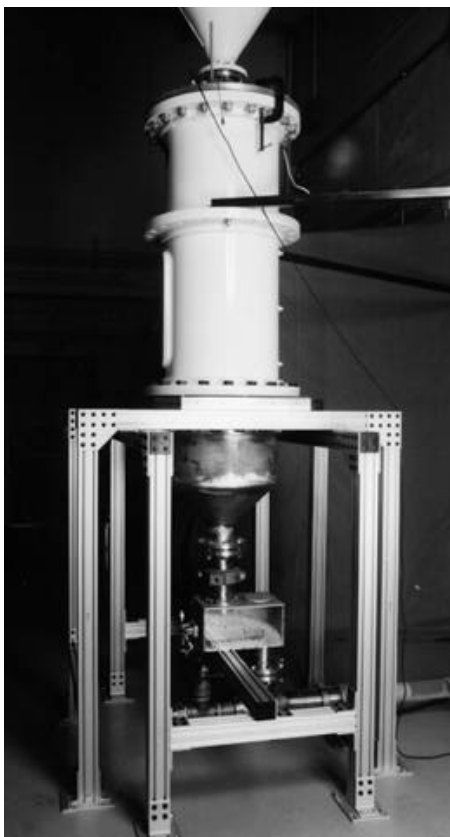

Figure 6. The cold-flow facility at Sandia National Laboratories–California. This unit is designed to simulate the processing of waste at a rate of 20 kg per hour, roughly ten times greater than that for our first demonstration tests at LLNL. Tests scheduled for later this year at the Sandia facility will further assess liquid–solid mixing requirements and evaluate the performance of a pneumatic conveyance system.

The Sandia facility is scaled to process material at a rate of approximately 20 kg per hour. This rate is about ten times larger than that for our first demonstration tests at LLNL and roughly ten times smaller than that required for a full-scale commercial unit.

We will use Sandia's cold-flow system to study various issues related to an increased mass-flow rate. A critical issue for any system that processes wastes containing radioactivity is ensuring its robustness and reliability. Once the unit itself becomes radioactive, maintenance becomes difficult, so it is desirable to eliminate mechanical complexity. Thus, the transport system, which includes the dispensing device (L-valve) and pneumatic lift, is a major issue in itself. The Sandia studies will include tests of the pneumatic transport system (with no moving parts) to circulate the ceramic spheres at a much larger scale than before.

The new tests will also look at another important issue: the liquid and solid mixing requirements in a ten-times larger system. We will study ways to inject the waste that avoid clogging of an injection nozzle as well as nonmechanical means to distribute the liquid over the ceramic spheres. These tests will improve our understanding of the overall process and enable us to identify the appropriate next steps toward the ultimate goal of a full-scale, stand-alone unit that can process waste at a rate of about 200 kg per hour.

Other Waste Treatment Applications of the HRS Process

The DOE is in the process of dismantling a large fraction of the nation's nuclear stockpile. One waste component from the dismantlement effort is chemical high explosives. The current method for disposing of high explosives is by open burning and open detonation. Regulatory agencies may soon greatly restrict or eliminate open burning and open detonation as ways to dispose of propellants, explosives, and pyrotechnics (also called PEPs). The DOE uses primarily plastic bonded explosive, or PBX for short. Although much of this material—as much as 90%—may be sold to industry, a certain amount will have to be destroyed. (Many other materials, such as solvents and wipes that come into contact with the high explosives, become classified as hazardous waste and will also have to be destroyed.) Some high explosives can be pretreated with sodium hydroxide in a process called base (or alkaline) hydrolysis. This process destroys that material's explosive nature, but the resulting liquid and gaseous products are still hazardous and thus require additional treatment.

New regulations require the military to examine the life cycle of any new PEP developed. The Army is currently evaluating disposal methods for a new liquid gun propellant, LP XM46, which is used as a conventional propellant for field artillery. This material is a mixture of hydroxyl-ammonium nitrate and triethanol-ammonium nitrate in 20% water. Liquid gun propellant is not detonable, and once diluted in a ratio of one to three with water, it is neither explosive nor flammable. Nevertheless, the material is chemically hazardous, and a suitable method, other than incineration, is needed to dispose of the liquid material.

We are exploring the use of the HRS process with hot ceramic spheres to destroy liquid gun propellant and the

The Hot-Recycled-Solid Process

Our hot-recycled-solid (HRS) process offers major improvements in efficiency and reliability over other processes for extracting oil from shale. Processing improvements of the type embodied by the HRS system hold the promise of making shale oil competitive with the world price of crude oil early in the next century.

In experiments during the mid-1980s, we constructed and operated a 1-tonne/day retort at LLNL to study the chemistry of oil shale pyrolysis. (Pyrolysis is the use of heat to break apart complex molecules into simpler units.) This retort produced oils with better stability and lower viscosity than previously thought possible. In 1990, we scaled up to a 4-tonne/day facility, which allowed us to study, for the first time, pyrolysis and combustion chemistry using the actual particle size (up to 7 mm) of commercial scale and to produce enough oil (about 10 gallons per run) for detailed characterization studies.

The major components of the HRS oil shale retorting process are shown in the illustration. First, raw crushed shale and recycled hot, spent shale are combined in a mixer. The mixed shale is pyrolyzed for 3 minutes in a moving packed-bed pyrolyzer to generate oil. Whole oil is then condensed for subsequent analysis and characterization. Whereas reaction temperatures are reached in less than a minute by our process, previous systems required 30 minutes to several hours. Rapid heatup promotes high product recovery with a 10 to 15% improvement over previous retorting methods. From a ton of Colorado shale, three quarters to one barrel of oil can typically be recovered.

Shale leaving the packed bed is lifted pneumatically to and through a delayed-fall combustor during which residual carbon is burned to provide the process heat. Solid waste is discharged from a fluid-bed classifier, which also serves as a pressure block that separates the reducing (heating) and oxidizing (burning) atmospheres. In an actual production plant, the oil would be refined into high-octane gasoline, jet fuel, or other petroleum products.

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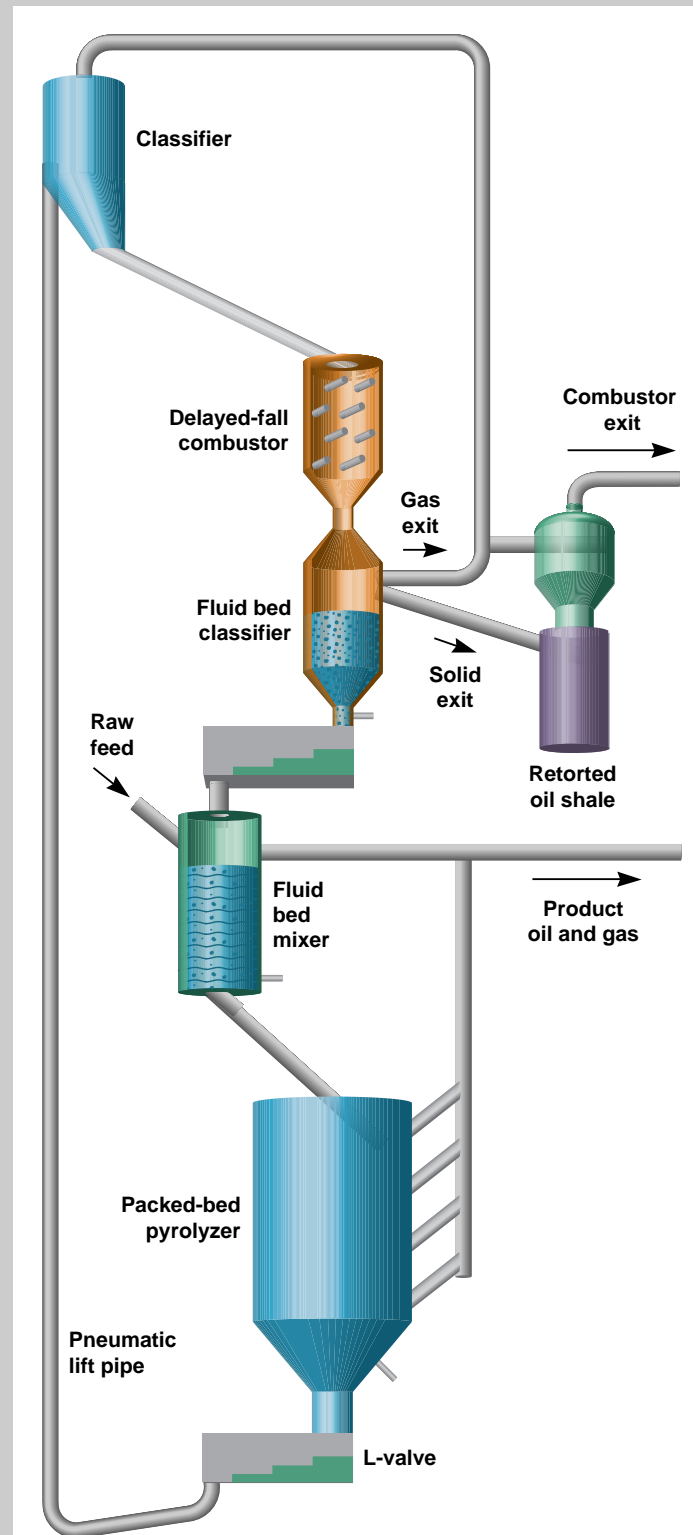
products from base hydrolysis of high explosives as an alternative to open burning and incineration. We have completed one run of each of the two materials in our modified HRS pilot plant to determine the gas products, condensable liquids, and solid products of decomposition. The HRS process destroyed the base hydrolysate and produced a small amount of solid material composed of 75% sodium carbonate and a small amount of aluminum oxide. Gaseous emissions of NO_x and other EPA-regulated pollutants were small.

We operated the HRS pilot plant 7 hours at steady-state conditions and destroyed 36 kg of diluted liquid gun propellant. Our experiments showed that this material was better destroyed in an oxidizing system (such as molten salt oxidation, reported in the January–February 1994 issue of *Energy and Technology Review*, pp. 42–43). Pyrolysis caused 8% of the nitrogen in the propellant to form oxides of nitrogen. Diversion of the gases to the lift section of the HRS and the addition of oxygen greatly reduced the nitrogen oxide formation. This work has already given us a good head-to-head comparison with other decomposition methods. More tests with the base hydrolysis products are planned in the near future.

The Road Ahead

At present, the DOE complex has no operational treatment or permanent disposal capability for mixed wastes—those containing both radioactive and chemically toxic substances. To meet this critical need, the Laboratory is designing a pilot facility to demonstrate integrated, end-to-end treatment of mixed waste. An existing building at LLNL has been assigned for this Mixed Waste Management Facility. Our HRS retort process is a potential core technology for this facility.

Before the HRS process can be used to clean up actual mixed waste, it must first undergo rigorous testing in a research and development mode. The Mixed Waste Management Facility provides the mechanism for developing promising new technologies in a facility permitted to handle and process mixed waste.

We also plan to collaborate with other LLNL researchers in the area of waste management. We will study ways the HRS process can be applied to treat the on-site mixed wastes that have been generated by Laboratory research and development. At present, LLNL researchers are looking at the HRS process and at steam reforming as one technique to handle the on-site mixed waste.

For further information please contact Robert J. Cena (510) 422-7336.